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Structures and magnetic properties of rare earth double perovskites containing antimony or bismuth Ba_2LnMO_6 (Ln =rare earths; M =Sb, Bi)

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ABSTRACT

A series of double perovskite-type oxides Ba_2LnMO_6 (Ln =lanthanides; M =Sb, Bi) were synthesized and their structures were studied. The Ln and M are structurally ordered in the rock-salt type at the B -site of the perovskite ABO_3 . For Ba_2PrBiO_6 and Ba_2TbBiO_6 , it has been found that the disordering between Ln ion and Bi ion occurs at the B -site of the double perovskite and both the Pr (Tb) and Bi exist in two oxidation state in the same compound from the analysis of the X-ray diffraction and magnetic susceptibility data. Magnetic susceptibility measurements show that all these compounds are paramagnetic and have no magnetic ordering down to 1.8 K.

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1. Introduction

The perovskite-type oxides have the general formula ABO_3 , in which A represents a large electropositive cation and B represents a small transition metal ions. They have often interesting physical properties, such as ferroelectricity, electrical conductivity, superconductivity, and magnetoresistance, due to their diversity of crystal structure and electronic properties.

We have been focusing our attention on the crystal structures of the perovskite-type oxides containing rare earth ions. The rare earth ion is relatively large and tends to adopt a high coordination number. Therefore, the rare earth ion usually sits at the A site of the perovskite-type oxides ABO_3 . Not the A site ions but the B site ions normally determine the physical properties of the perovskites [1]. The perovskites have the flexibility of chemical composition and the possibility of combination of many kinds of ions. By selecting large alkaline earth elements such as Ba at the A site atoms, one finds that the rare earths occupy the 6-coordinate B sites. Double perovskite-type oxides have the formula $A_2B'B''O_6$, in which the primes indicate the different ions in different oxidation states, and the cations at the B -sites, B' and B'' , are regularly ordered, i.e., 1:1 arrangement of B' and B'' ions has been observed over the six-coordinate B sites. Different kinds of B' and B'' ion

should show a variety of the physical properties of double perovskite oxides. Since highly oxidized cations from the second or third transition series sometimes show quite unusual magnetic behavior, many studies have been performed on the preparation and magnetic properties of double perovskite oxides containing both rare earth and such transition metals, A_2LnMO_6 (A =Sr, Ba; Ln =rare earths; M =Ru, Os, Ir, Re) [2–19].

On the other hand, studies on double perovskites containing post-transition elements such as antimony and bismuth, Ba_2LnMO_6 (M =Sb, Bi), are very limited. Structures of Ba_2LnSbO_6 (Ln =La, Pr, Nd, Sm) were investigated by X-ray and neutron diffraction measurements [20,21]. Harrison et al. reported structures and magnetic properties of Ba_2LnBiO_6 (Ln =Ce, Pr, Nd, Tb) [22]. In this study, we have paid our attention to the structural chemistry and magnetic properties of such double perovskites. From the standpoint of the crystal chemistry, this series of rare earth compounds are suitable to systematically study their crystal structures. The valence states of the Ln and Sb (Bi) ions are expected to be trivalent ($[Xe]4f^n$) and pentavalent ($[Kr]4d^{10}$, $[Xe]5d^{10}$), respectively ($[Xe]$: electronic xenon core, $[Kr]$: electronic krypton core). Therefore, the magnetic behavior of this series of compounds depends only on Ln^{3+} ions. That is, this system is appropriate for the study of the magnetic behavior of f -electrons at the B sites of double perovskites. The aim of the present work is to prepare a series of Ba_2LnMO_6 (M =Sb, Bi) compounds with different rare earths and to investigate the influence of the size of the Ln cations on the stability of the structure and their

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magnetic properties through measurements of the powder X-ray diffraction and the magnetic susceptibilities in detail. Measurements of the ^{151}Eu Mössbauer spectra were also performed for Ba_2EuMO_6 ($M=\text{Sb, Bi}$) compounds.

2. Experimental

2.1. Sample preparation

Polycrystalline samples of double perovskites Ba_2LnMO_6 ($\text{Ln}=\text{rare earths}$; $M=\text{Sb, Bi}$) were prepared by the standard solid-state reaction. Barium carbonate BaCO_3 , rare earth sesqui-oxides Ln_2O_3 ($\text{Ln}=\text{Y, La, Nd, Sm-Gd, Dy-Lu}$), antimony sesqui-oxide Sb_2O_3 , and bismuth sesqui-oxide Bi_2O_3 were used as starting materials. For the case of Pr and Tb, Pr_6O_{11} and Tb_4O_7 were used. The rare earth oxides and barium carbonate were dried prior to use by heating overnight at 1000 and 100 °C, respectively. These starting materials were well mixed in an agate mortar. The mixtures were pressed into pellets and heated in air at 1300 °C for 20 h. The pellets were reground, repressed, and reheated in the same condition. These heating procedures were repeated several times.

2.2. X-ray diffraction analysis

Powder X-ray diffraction profiles were measured using a Rigaku Multi-Flex diffractometer with $\text{CuK}\alpha$ radiation equipped

with a curved graphite monochromator. The data were collected by step-scanning in the angle range of $10^\circ \leq 2\theta \leq 120^\circ$ at a 2θ step-size of 0.02° . The X-ray diffraction data were analyzed by the Rietveld technique, using the program RIETAN-FP [23] and the crystal structure was drawn by VESTA program [24].

2.3. Magnetic susceptibility measurements

The temperature-dependence of the magnetic susceptibility was measured in an applied field of 0.1 T over the temperature range of $1.8 \text{ K} \leq T \leq 300 \text{ K}$, using a SQUID magnetometer (Quantum Design, MPMS5S). The susceptibility measurements were performed under both zero-field-cooled (ZFC) and field-cooled (FC) conditions. The former was measured upon heating the sample to 300 K under the applied magnetic field of 0.1 T after zero-field cooling to 1.8 K. The latter was measured upon cooling the sample from 300 to 1.8 K in the applied field of 0.1 T.

2.4. ^{151}Eu Mössbauer spectrum measurements

The ^{151}Eu Mössbauer spectra were measured with a Mössbauer spectrometer VT-6000 (Laboratory Equipment Co.) in the constant acceleration mode using a radiation source $^{151}\text{SmF}_3$ (1.85 GBq). The spectrometer was calibrated with a spectrum of $\alpha\text{-Fe}$ at room temperature. The γ -rays were detected with a NaI scintillation counter. Europium trifluoride (EuF_3) was used as a reference standard for the chemical isomer shift. The sample was wrapped in an

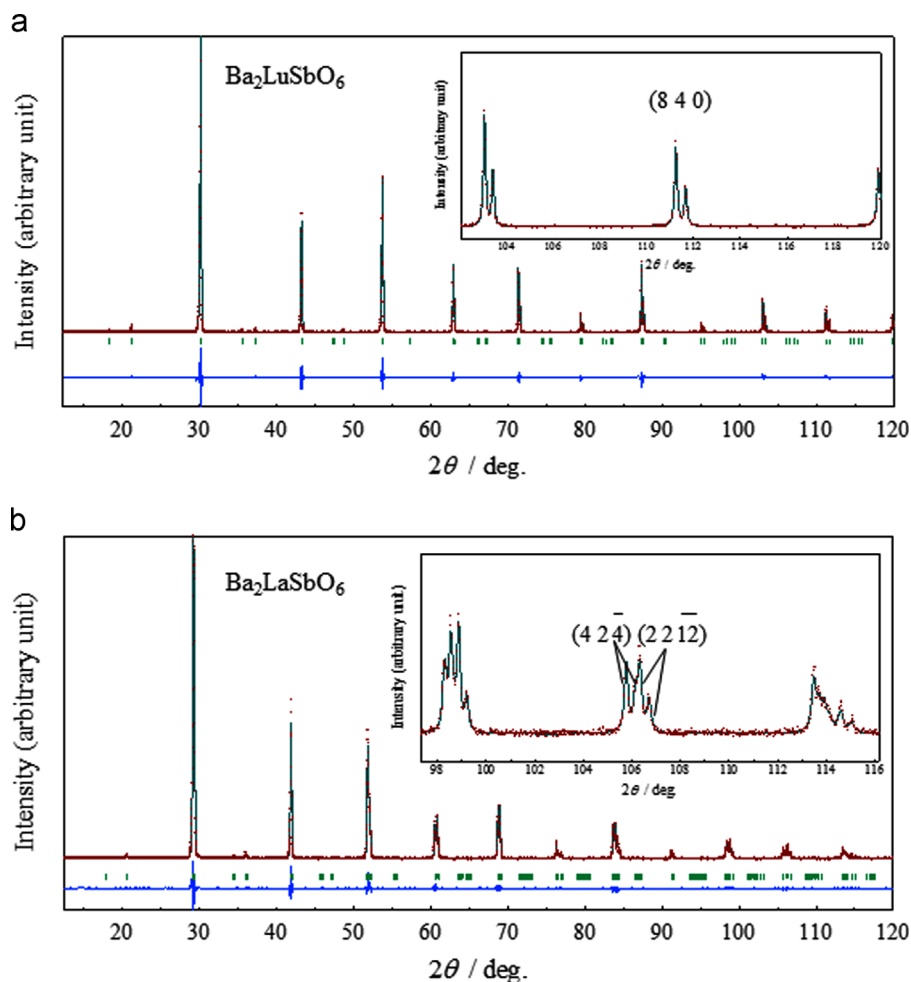


Fig. 1. Powder X-ray diffraction profiles for (a) $\text{Ba}_2\text{LuSbO}_6$ and (b) $\text{Ba}_2\text{LaSbO}_6$. The calculated profiles based on the $Fm\bar{3}m$ (for $\text{Ba}_2\text{LuSbO}_6$) or $R\bar{3}$ (for $\text{Ba}_2\text{LaSbO}_6$) model and the observed profiles are shown on the top solid line and cross markers, respectively. The vertical marks in the middle show positions calculated for Bragg reflections. The lower trace is a plot of the difference between calculated and observed intensities. The insets show the enlarged diffraction profiles in high 2θ region.

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